# APPENDIX C
# MEASUREMENT QUALITY OBJECTIVES FOR METHOD UNCERTAINTY AND DETECTION AND QUANTIFICATION CAPABILITY

## C.1 Introduction

This appendix expands on issues related to measurement quality objectives (MQOs) for several method performance characteristics which are introduced in Chapter 3, *Key Analytical Planning Issues and Developing Analytical Protocol Specifications*. Specifically, this appendix provides the rationale and guidance for establishing project-specific MQOs for the following method performance characteristics: method uncertainty, detection capability and quantification capability. In addition, it provides guidance in the development of these MQOs for use in the method selection process and guidance in the evaluation of laboratory data based on the MQOs. Section C.2 is a brief overview of statistical hypothesis testing as it is commonly used in a directed planning process, such as the Data Quality Objectives (DQO) Process (EPA 2000). More information on this subject is provided in Chapter 2, *Directed Planning Process* and Appendix B, *The Data Quality Objectives Process*. Section C.3 derives MARLAP's recommended criteria for establishing project-specific MQOs for method uncertainty, detection capability, and quantification capability. These criteria for method selection will meet the requirements of a statistically based decision-making process. Section C.4 derives MARLAP's recommended criteria for evaluation of the results of quality control analyses by project managers and data reviewers (see also Chapter 8, *Radiochemical Data Verification and Validation*).

It is assumed that the reader is familiar with the concepts of measurement uncertainty, detection capability, and quantification capability, and with terms such as "standard uncertainty," "minimum detectable concentration," and "minimum quantifiable concentration," which are introduced in Chapter 1, *Introduction to MARLAP*, and discussed in more detail in Chapter 19, *Measurement Statistics*. MARLAP also uses the term "method uncertainty" to refer to the predicted uncertainty of the result that would be measured if the method were applied to a hypothetical laboratory sample with a specified analyte concentration. The method uncertainty is a characteristic of the analytical method and the measurement process.

## C.2 Hypothesis Testing

Within the framework of a directed planning process, one considers an *action level*, denoted here by AL, which is the contaminant concentration in either a population (e.g., a survey unit) or an individual item (e.g., a laboratory sample) that should not be exceeded. Statistical hypothesis testing is used to decide whether the actual contaminant concentration $X$ is greater than AL. For more information on this topic, see EPA QA/G-4, MARSSIM, NUREG-1505 (EPA 2000, MARSSIM 2000, NRC 1998), or Appendix B of this manual.

In hypothesis testing, one formulates two hypotheses about the value of $X$, and evaluates the measurement data to choose which hypothesis to accept and which to reject.[1] The two hypotheses are called the *null hypothesis* $H_0$ and the *alternative hypothesis* $H_1$. They are mutually exclusive and together describe all possible values of $X$ under consideration. So, in any given situation, one and only one of the hypotheses must be true. The null hypothesis is presumed true unless the data provide evidence to the contrary. Thus the choice of the null hypothesis determines the burden of proof in the test.

Most often, if the action level is not zero, one assumes it has been exceeded unless the measurement results provide evidence to the contrary. In this case, the null hypothesis is $H_0$: $X \geq \text{AL}$ and the alternative hypothesis is $H_1$: $X < \text{AL}$. If one instead chooses to assume the action level has not been exceeded unless there is evidence to the contrary, then the null hypothesis is $H_0$: $X \leq \text{AL}$ and the alternative hypothesis is $H_1$: $X > \text{AL}$. The latter approach is the only reasonable one if AL = 0, because it is virtually impossible to obtain statistical evidence that an analyte concentration is exactly zero.

In any hypothesis test, there are two possible types of decision errors. A *Type I* error occurs if the null hypothesis is rejected when it is, in fact, true. A *Type II* error occurs if the null hypothesis is not rejected when it is false.[2] Since there is always measurement uncertainty, one cannot eliminate the possibility of decision errors. So instead, one specifies the maximum Type I decision error rate $\alpha$ that is allowable when the contaminant concentration is at or above the action

---

[1] In hypothesis testing, to "accept" the null hypothesis only means not to reject it, and for this reason many statisticians avoid the word "accept" in this context. A decision not to reject the null hypothesis does not imply the null hypothesis has been shown to be true.

[2] The terms "false positive" and "false negative" are synonyms for "Type I error" and "Type II error," respectively. However, MARLAP deliberately avoids these terms here, because they may be confusing when the null hypothesis is an apparently "positive" statement, such as $X \geq \text{AL}$.

level AL. This maximum usually occurs when the concentration is exactly equal to AL. The most commonly used value of $\alpha$ is 0.05, or 5%. One also chooses another concentration DL (the "discrimination limit") that one wishes to be able to distinguish reliably from the action level. One specifies the maximum Type II decision error rate $\beta$ that is allowable when the contaminant concentration equals DL, or, equivalently, the "power" $1 - \beta$ of the statistical test at $X = \text{DL}$. The *gray region* is then defined as the interval between the two concentrations AL and DL.

The gray region is a set of concentrations close to the action level, where one is willing to tolerate a Type II decision error rate that is higher than $\beta$. For concentrations above the upper bound of the gray region or below the lower bound, the decision error rate is no greater than the specified value (either $\alpha$ or $\beta$ as appropriate). Ideally, the gray region should be narrow, but in practice, its width is determined by balancing the costs involved, including the cost of measurements and the estimated cost of a Type II error, possibly using prior information about the project and the parameter being measured.

If $H_0$ is $X \geq \text{AL}$ (presumed contaminated), then the upper bound of the gray region is AL and the lower bound is DL. If $H_0$ is $x \leq \text{AL}$ (presumed uncontaminated), then the lower bound of the gray region is AL and the upper bound is DL. Since no assumption is made here about which form of the null hypothesis is being used, the lower and upper bounds of the gray region will be denoted by LBGR and UBGR, respectively, and not by AL and DL. The width of the gray region (UBGR – LBGR) is denoted by $\Delta$ and called the *shift* or the required *minimum detectable difference* in concentration (EPA 2000, MARSSIM 2000, NRC 1998). See Appendix B, *The Data Quality Objectives Process*, for graphical illustrations of these concepts.

Chapter 3 of MARLAP recommends that for each radionuclide of concern, an action level, gray region, and limits on decision error rates be established during a directed planning process. Section C.3 presents guidance on the development of MQOs for the selection and development of analytical protocols. Two possible scenarios are considered. In the first scenario, the parameter of interest is the mean analyte concentration for a sampled population. The question to be answered is whether the population mean is above or below the action level. In the second scenario a decision is to be made about individual items or specimens, and not about population parameters. This is the typical scenario in bioassay, for example. Some projects may involve both scenarios. For example, project planners may want to know whether the mean analyte concentration in a survey unit is above an action level, but they may also be concerned about individual samples with high analyte concentrations.

## C.3 Development of MQOs for Analytical Protocol Selection

This section derives MARLAP's recommendations for establishing MQOs for the analytical protocol selection and development process. Guidance is provided for establishing project-specific MQOs for method uncertainty, detection capability, and quantification capability. Once selected, these MQOs are used in the initial, ongoing, and final evaluations of the protocols. MARLAP considers two scenarios and develops MQOs for each.

**SCENARIO I: A Decision Is to Be Made about the Mean of a Sampled Population**

In this scenario the total variance of the data $\sigma^2$ is the sum of two components

$$\sigma^2 = \sigma_M^2 + \sigma_S^2$$

where $\sigma_M^2$ is the average analytical method variance ($M$ = "method") and $\sigma_S^2$ is the variance of the sampled population. The sampling standard deviation $\sigma_S$ may be affected by the spatial and temporal distribution of the analyte, the extent of the survey unit, the physical sample sizes, and the sample collection procedures. The analytical standard deviation $\sigma_M$ is affected by laboratory sample preparation, subsampling, and analysis procedures. The value of $\sigma_M$ may be estimated by the *combined standard uncertainty* of a measured value for a sample whose concentration equals the hypothesized population mean concentration (see Chapter 19, *Measurement Statistics*).

The ratio $\Delta / \sigma$, called the "relative shift," determines the number of samples required to achieve the desired decision error rates $\alpha$ and $\beta$. The target value for this ratio should be between 1 and 3, as explained in MARSSIM and NUREG-1505 (MARSSIM 2000, NRC 1998). Ideally, to keep the required number of samples low, one prefers that $\Delta / \sigma \approx 3$. The cost in number of samples rises rapidly as the ratio $\Delta / \sigma$ falls below 1, but there is little benefit from increasing the ratio much above 3.

Generally, it is easier to control $\sigma_M$ than $\sigma_S$. If $\sigma_S$ is known (approximately), a target value for $\sigma_M$ can be determined. For example, if $\sigma_S < \Delta / 3$, then a value of $\sigma_M$ no greater than $\sqrt{\Delta^2 / 9 - \sigma_S^2}$ ensures that $\sigma \le \Delta / 3$, as desired. If $\sigma_S > \Delta / 3$, the requirement that the total $\sigma$ be less than $\Delta / 3$ cannot be met regardless of $\sigma_M$. In the latter case, it is sufficient to make $\sigma_M$ negligible in comparison to $\sigma_S$.

Often one needs a method for choosing $\sigma_M$ in the absence of specific information about $\sigma_S$. In this situation, MARLAP recommends the requirement $\sigma_M \le \Delta / 10$ by default. The recommendation is justified below.

Since it is desirable to have $\sigma \leq \Delta / 3$, this condition is adopted as a primary requirement. Assume for the moment that $\sigma_S$ is large. Then $\sigma_M$ should be made negligible by comparison. Generally, $\sigma_M$ is considered negligible if it is no greater than about $\sigma_S / 3$. When this condition is met, further reduction of $\sigma_M$ has little effect on $\sigma$ and therefore is usually not cost-effective. So, the inequality $\sigma_M \leq \sigma_S / 3$ is adopted as a second requirement.

Algebraic manipulation of the equation $\sigma^2 = \sigma_M^2 + \sigma_S^2$ and the required inequality $\sigma_M \leq \sigma_S / 3$ gives

$$\sigma_M \leq \frac{\sigma}{\sqrt{10}}$$

The inequalities $\sigma \leq \Delta / 3$ and $\sigma_M \leq \sigma / \sqrt{10}$ together imply the requirement

$$\sigma_M \leq \frac{\Delta}{3\sqrt{10}}$$

or approximately

$$\sigma_M \leq \frac{\Delta}{10}$$

The required upper bound for the standard deviation $\sigma_M$ will be denoted by $\sigma_{MR}$. MARLAP recommends

$$\sigma_{MR} = \frac{\Delta}{10}$$

by default as a requirement in Scenario I when $\sigma_S$ is unknown. This upper bound was derived from the assumption that $\sigma_S$ was large, but it also ensures that the primary requirement $\sigma \leq \Delta / 3$ will be met if $\sigma_S$ is small. When the analytical standard deviation $\sigma_M$ is less than $\sigma_{MR}$, the primary requirement will be met unless the sampling variance $\sigma_S^2$ is so large that $\sigma_M^2$ is negligible by comparison, in which case little benefit can be obtained from further reduction of $\sigma_M$.

The recommended value of $\sigma_{MR}$ is based on the assumption that any known bias in the measurement process has been corrected and that any remaining bias is much smaller than the shift, $\Delta$, when a concentration near the gray region is measured.

Achieving an analytical standard deviation $\sigma_M$ less than the recommended limit, $\Delta / 10$, may be difficult in some situations, particularly when the shift, $\Delta$, is only a fraction of UBGR. When the recommended requirement for $\sigma_M$ is too costly to meet, project planners may allow $\sigma_{MR}$ to be larger, especially if $\sigma_S$ is believed to be small or if it is not costly to analyze the additional samples required because of the larger overall data variance ($\sigma_M^2 + \sigma_S^2$). In this case, project planners may choose $\sigma_{MR}$ to be as large as $\Delta$ / 3 or any calculated value that allows the data quality objectives to be met at an acceptable cost.

The true standard deviation, $\sigma_M$, is a theoretical quantity and is never known exactly, but the laboratory may estimate its value using the methods described in Chapter 19, and Section 19.6.13 in particular. The laboratory's estimate of $\sigma_M$ will be denoted here by $u_M$ and called the "method uncertainty." The method uncertainty, when estimated by uncertainty propagation, is the predicted value of the combined standard uncertainty ("one-sigma" uncertainty) of the analytical result for a laboratory sample whose concentration equals UBGR. Note that the term "method uncertainty" and the symbol $u_M$ actually apply not only to the method but to the entire measurement process.

In theory, the value $\sigma_{MR}$ is intended to be an upper bound for the true standard deviation of the measurement process, $\sigma_M$, which is unknown. In practice, $\sigma_{MR}$ is actually used as an upper bound for the method uncertainty, $u_M$, which may be calculated. Therefore, the value of $\sigma_{MR}$ will be called the "required method uncertainty" and denoted by $u_{MR}$. As noted in Chapter 3, MARLAP recommends that project planners specify an MQO for the method uncertainty, expressed in terms of $u_{MR}$, for each analyte and matrix.

The MQO for method uncertainty is expressed above in terms of the required standard deviation of the measurement process for a laboratory sample whose analyte concentration is at or above the upper bound of the gray region, UBGR. In principle the same MQO may be expressed as a requirement that the minimum quantifiable concentration (MQC) be less than or equal to UBGR. Chapter 19 defines the MQC as the analyte concentration at which the relative standard deviation of the measured value (i.e., the relative method uncertainty) is 1 / $k_Q$, where $k_Q$ is some specified positive value. The value of $k_Q$ in this case should be specified as $k_Q$ = UBGR / $u_{MR}$. In fact, if the lower bound of the gray region is zero, then one obtains $k_Q$ = 10, which is the value most commonly used to define the MQC in other contexts. In practice the requirement for method uncertainty should only be expressed in terms of the MQC when $k_Q$ = 10, since to define the MQC with any other value of $k_Q$ may lead to confusion.

**EXAMPLE:** Suppose the action level is 1 Bq/kg and the lower bound of the gray region is 0.6 Bq/kg. If decisions are to be made about survey units based on samples, then the required method uncertainty at 1 Bq/kg is

$$u_{MR} = \frac{\Delta}{10} = \frac{1 - 0.6}{10} = 0.04 \text{ Bq/kg}$$

If this uncertainty cannot be achieved, then an uncertainty as large as $\Delta$ / 3 = 0.13 Bq/kg may be allowed if $\sigma_S$ is small or if more samples are taken per survey unit.

A common practice in the past has been to select an analytical method based on the *minimum detectable concentration* (MDC), which is defined in Chapter 19, *Measurement Statistics*. For example, the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM 2000) says:

> During survey design, it is generally considered good practice to select a measurement system with an MDC between 10-50% of the DCGL [action level].

Such guidance implicitly recognizes that for cases when the decision to be made concerns the mean of a population that is represented by multiple laboratory samples, criteria based on the MDC may not be sufficient and a somewhat more stringent requirement is needed. It is interesting to note that the requirement that the MDC (about 3 times $\sigma_M$) be 10–50% of the action level is tantamount to requiring that $\sigma_M$ be 0.03 to 0.17 times the action level — i.e. the relative standard deviation should be approximately 10% at the action level. Thus, the requirement is more naturally expressed in terms of the MQC.

**SCENARIO II: Decisions Are to Be Made about Individual Items**

In this scenario, the total variance of the data equals the analytical variance, $\sigma_M^2$. Consequently the data distribution in most instances should be approximately normal. The decision in this case may be made by comparing the measured concentration, $x$, plus or minus a multiple of its combined standard uncertainty to the action level, AL. The combined standard uncertainty, $u_c(x)$, is assumed to be an estimate of the true standard deviation of the measurement process as applied to the item being measured; so, the multiplier of $u_c(x)$ equals $z_{1-\alpha}$, the $(1 - \alpha)$-quantile of the standard normal distribution (see Appendix G, *Statistical Tables*).

Alternatively, if AL is zero, so that any detectable amount of analyte is of concern, the decision may involve comparing $x$ to the critical value of the concentration, $x_C$, as defined in Chapter 19, *Measurement Statistics*.

**Case II-1:** Suppose the null hypothesis is $x \geq$ AL, so that the action level, AL, equals the upper bound of the gray region, UBGR. Given the analytical variance $\sigma_M^2$, only a measured result that is less than about UBGR – $z_{1-\alpha}\sigma_M$ will be judged to be clearly less than the action level. Then the desired power of the test 1 – β is achieved at the lower bound of the gray region only if LBGR ≤ UBGR – $z_{1-\alpha}\sigma_M - z_{1-\beta}\sigma_M$. Algebraic manipulation transforms this requirement to

$$\sigma_M \leq \frac{\text{UBGR} - \text{LBGR}}{z_{1-\alpha} + z_{1-\beta}} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

**Case II-2:** Suppose the null hypothesis is $x \leq$ AL, so that the action level, AL, equals the lower bound of the gray region, LBGR. Then only a measured result that is greater than about LBGR + $z_{1-\alpha}\sigma_M$ will be judged to be clearly greater than the action level. Then the desired power of the test 1 – β is achieved at the upper bound of the gray region only if UBGR ≥ LBGR + $z_{1-\alpha}\sigma_M$ + $z_{1-\beta}\sigma_M$. Algebraic manipulation transforms this requirement to

$$\sigma_M \leq \frac{\text{UBGR} - \text{LBGR}}{z_{1-\alpha} + z_{1-\beta}} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

So, in either case, we have the requirement:

$$\sigma_M \leq \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

Therefore, MARLAP recommends the use of

$$u_{MR} = \sigma_{MR} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

as an MQO for method uncertainty when decisions are to be made about individual items (i.e., laboratory samples) and not about population parameters.

If both $\alpha$ and $\beta$ are at least 0.05, one may use the value $u_{MR} = 0.3\Delta$.

If LBGR = 0, then $\Delta$ = UBGR and $\sigma_{MR} = \Delta / (z_{1-\alpha} + z_{1-\beta})$ implies

$$\sigma_M \leq \frac{\text{UBGR}}{z_{1-\alpha} + z_{1-\beta}}$$

This requirement is essentially equivalent to requiring that the MDC not exceed UBGR. Thus, when LBGR = 0, the MQO may be expressed in terms of the detection capability of the analytical method.

Note that when AL = LBGR = 0, the MQO for detection capability may be derived directly in terms of the MDC, since the MDC is defined as the analyte concentration at which the probability of detection is $1 - \beta$ when the detection criterion is such that the probability of false detection in a sample with zero analyte concentration is at most $\alpha$.

**EXAMPLE:** Suppose the action level is 1 Bq/L, the lower bound of the gray region is 0.5 Bq/L, $\alpha = 0.05$, and $\beta = 0.10$. If decisions are to be made about individual items, then the required method uncertainty at 1 Bq/L is

$$u_{MR} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}} = \frac{1 - 0.5}{z_{0.95} + z_{0.90}} = \frac{0.5}{1.645 + 1.282} = 0.17 \text{ Bq/L}.$$

## C.4 The Role of the MQO for Method Uncertainty in Data Evaluation

This section provides guidance and equations for determining warning and control limits for QC sample results based on the project-specific MQO for method uncertainty. In the MARLAP Process as described in Chapter 1, these warning and control limits are used in the ongoing evaluation of protocol performance (see Chapter 7, *Evaluating Protocols and Laboratories*) and in the evaluation of the laboratory data (see Chapter 8, *Radiochemical Data Verification and Validation).*

### C.4.1 Uncertainty Requirements at Various Concentrations

When project planners follow MARLAP's recommendations for establishing MQOs for method uncertainty for method selection and development, the maximum allowable standard deviation,

$\sigma_{MR}$, at the upper bound of the gray region (UBGR) is specified. During subsequent data evaluation, the standard deviation at any concentration less than UBGR should be at most $\sigma_{MR}$, and the relative standard deviation at any concentration greater than UBGR should be at most $\sigma_{MR}$ / UBGR, which will be denoted here by $\varphi_{MR}$. Note that, since the true standard deviation can never be known exactly, in practice the requirement is expressed in terms of the required method uncertainty, $u_{MR}$, to which the combined standard uncertainty of each result may be compared.

**EXAMPLE:** Consider the preceding example, in which AL = UBGR = 1 Bq/L, LBGR = 0.5 Bq/L, and $u_{MR}$ = 0.17 Bq/L. In this case the combined standard uncertainty for any measured result $x$ should be at most 0.17 Bq/L if $x$ < 1 Bq/L, and the relative combined standard uncertainty should be at most 0.17 / 1, or 17%, if $x$ > 1 Bq/L.

In Scenario I, where decisions are made about the mean of a population based on multiple physical samples (e.g., from a survey unit), if the default value $\sigma_{MR} = \Delta / 10$ is assumed for the required method uncertainty, then the required bound for the analytical standard deviation as a function of concentration is as shown in Figure C.1 below. The figure shows that the bound, $\sigma_{\text{Req}}$, is constant at all concentrations, $x$, below UBGR, and $\sigma_{\text{Req}}$ increases with $x$ when $x$ is above UBGR. So, $\sigma_{\text{Req}} = \sigma_{MR}$ when $x$ < UBGR and $\sigma_{\text{Req}} = x \cdot \sigma_{MR}$ / UBGR when $x$ > UBGR.

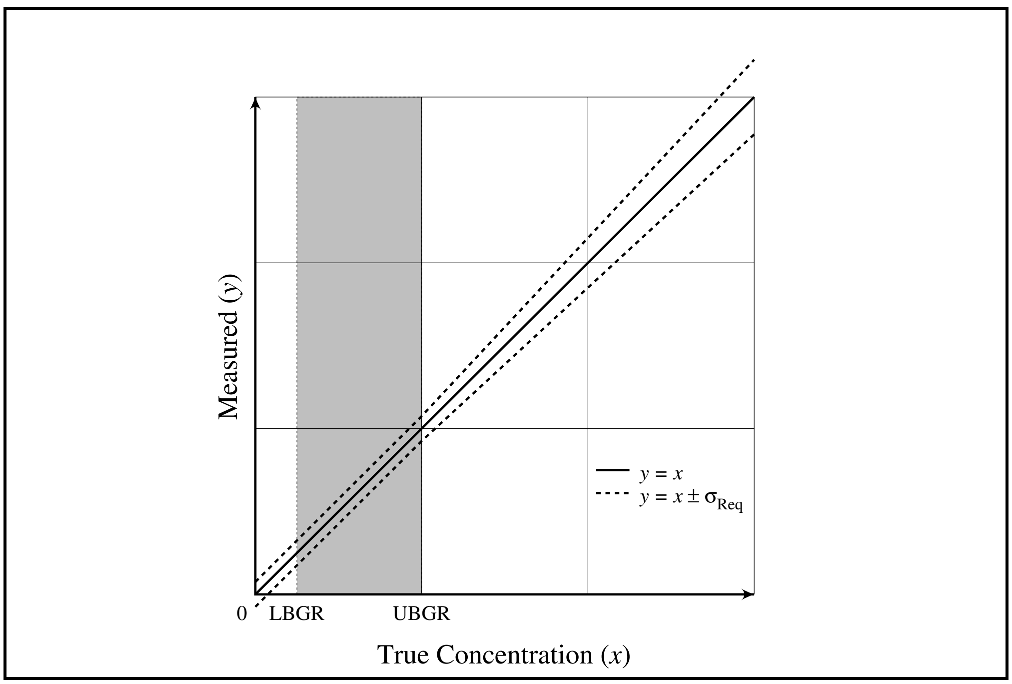


**FIGURE C.1 — Required Analytical Standard Deviation ($\sigma_{\text{Req}}$)**

These requirements can be relaxed somewhat for samples with very high analyte concentrations as long as the project's requirements for decision uncertainty are met. However, MARLAP does not provide specific guidance to address this issue for Scenario I.

In Scenario II, where decisions are made about individual physical samples, it is possible to widen the required bounds for the standard deviation at any concentration outside the gray region. For example, suppose the upper bound of the gray region (UBGR) is at the action level (AL), the lower bound (LBGR) is set at some concentration below UBGR, and the decision error probabilities $\alpha$ and $\beta$ are specified. Then the project planners require the probability of a Type I error not to exceed $\alpha$ when the true concentration is at or above UBGR, and they require the probability of a Type II error not to exceed $\beta$ when the true concentration is at or below LBGR. The decision rule is based on the combined standard uncertainty of the measurement result: any sample whose measured concentration, $x$, exceeds AL minus $z_{1-\alpha}$ times the combined standard uncertainty, $u_c(x)$, is assumed to exceed the action level. So, assuming $u_c(x)$ is an adequate estimate of the analytical standard deviation, the planners' objectives are met if

$$u_c(x) \le \begin{cases} \dfrac{\mathrm{UBGR} - x}{z_{1-\alpha} + z_{1-\beta}}, & \text{if } x \le \mathrm{LBGR} \\ \dfrac{x - \mathrm{LBGR}}{z_{1-\alpha} + z_{1-\beta}}, & \text{if } x \ge \mathrm{UBGR} \\ \dfrac{\Delta}{z_{1-\alpha} + z_{1-\beta}}, & \text{if } \mathrm{LBGR} \le x \le \mathrm{UBGR} \end{cases}$$

**EXAMPLE:** Consider the earlier example in which AL = UBGR = 1.0 Bq/L, LBGR = 0.5 Bq/L, $\alpha = 0.05$, $\beta = 0.10$, and $u_{MR} = 0.17$ Bq/L. The less restrictive uncertainty requirement can be expressed as

$$u_c(x) \le \begin{cases} \dfrac{1.0 - x}{2.927}, & \text{if } x \le 0.5\ \mathrm{Bq/L} \\ \dfrac{x - 0.5}{2.927}, & \text{if } x \ge 1.0\ \mathrm{Bq/L} \\ 0.17, & \text{if } 0.5\ \mathrm{Bq/L} \le x \le 1.0\ \mathrm{Bq/L} \end{cases}$$

So, if $x = 0$, the requirement is $u_c(x) \le 1 / 2.927 = 0.34$ Bq/L, and, if $x = 2$, the requirement is $u_c(x) \le (2 - 0.5) / 2.927 = 0.51$ Bq/L, which is approximately 26% in relative terms.

### C.4.2 Acceptance Criteria for Quality Control Samples

The next issue to be addressed is how to set warning and control limits for quality control (QC) sample results. These limits will be used by project data assessors to determine whether the laboratory appears to be meeting MQOs. Presumably the lab has stricter internal QC requirements (see Chapter 18, *Laboratory Quality Control*).

The development of acceptance criteria for QC samples will be illustrated with an example. Assume the upper bound of the gray region (UBGR) is 5 Bq/kg (soil) and the lower bound of the gray region (LBGR) is 1.5 Bq/kg. The width of the gray region is $\Delta = 5 - 1.5 = 3.5$ Bq/kg. Project planners, following MARLAP's guidance, choose the required method uncertainty at 5 Bq/kg (UBGR) to be

$$u_{MR} = \frac{\Delta}{10} = 0.35\ \mathrm{Bq/kg}$$

or 7%. So, the maximum standard uncertainty at analyte concentrations less than 5 Bq/kg should be $u_{MR} = 0.35$ Bq/kg, and the maximum *relative* standard uncertainty at concentrations greater than 5 Bq/kg should be $\varphi_{MR} = 0.07$, or 7%.

Although it is possible to relax these uncertainty criteria for samples with very high analyte concentrations, MARLAP recommends that the original criteria be used to develop acceptance limits for the results of QC sample analyses.

#### C.4.2.1 Laboratory Control Samples

It is assumed that the concentration of a laboratory control sample (LCS) is high enough that the relative uncertainty limit $\varphi_{MR} = 0.07$ is appropriate. The *percent deviation* for the LCS analysis is defined as

$$\%D = \frac{\mathrm{SSR} - \mathrm{SA}}{\mathrm{SA}} \times 100\%$$

where

SSR is the measured result (spiked sample result) and
SA is the spike activity (or concentration) added.

It is assumed that the uncertainty of SA is negligible; so, the maximum allowable relative standard deviation of $\%D$ is the same as that of the measured result itself, or $\varphi_{MR} \times 100\%$. Then the 2-

sigma warning limits for $\%D$ are $\pm 2\varphi_{MR} \times 100\%$ and the 3-sigma control limits are $\pm 3\varphi_{MR} \times 100\%$. (In situations where $\varphi_{MR}$ is very small, the uncertainty of SA should not be ignored.)

The requirements for LCSs are summarized below.

**Laboratory Control Samples**

Statistic: $$\%D = \frac{\text{SSR} - \text{SA}}{\text{SA}} \times 100\%$$

Warning limits: $\pm 2\varphi_{MR} \times 100\%$

Control limits: $\pm 3\varphi_{MR} \times 100\%$

**EXAMPLE**

(UBGR = 5 Bq/kg, $u_{MR}$ = 0.35 Bq/kg, $\varphi_{MR}$ = 0.07.)

Suppose an LCS is prepared with a concentration of SA = 10 Bq/kg and the result of the analysis is 11.61 Bq/kg with a combined standard uncertainty of 0.75 Bq/kg. Then

$$\%D = \frac{11.61 - 10}{10} \times 100\% = 16.1\%$$

The warning limits in this case are

$$\pm 2\varphi_{MR} \times 100\% = \pm 14\%$$

and the control limits are

$$\pm 3\varphi_{MR} \times 100\% = \pm 21\%$$

So, the calculated value of $\%D$ is above the upper warning limit but below the control limit.

C.4.2.2 Duplicate Analyses

Acceptance criteria for duplicate analysis results depend on the sample concentration, which is estimated by the average $\bar{x}$ of the two measured results $x_1$ and $x_2$.

$$\bar{x} = \frac{x_1 + x_2}{2}$$

When $\bar{x}$ < UBGR, the warning limit for the absolute difference $|x_1 - x_2|$ is

$$2\,u_{MR}\sqrt{2} \approx 2.83\ u_{MR}$$

and the control limit is

$$3\,u_{MR}\sqrt{2} \approx 4.24\ u_{MR}$$

Only upper limits are used, because the absolute value $|x_1 - x_2|$ is being tested.

When $\bar{x} \geq$ UBGR, the acceptance criteria may be expressed in terms of the *relative percent difference* (RPD), which is defined as

$$\text{RPD} = \frac{|x_1 - x_2|}{\bar{x}} \times 100\%$$

The warning limit for RPD is

$$2\varphi_{MR}\sqrt{2} \times 100\% \approx 2.83\ \varphi_{MR} \times 100\%$$

and the control limit is

$$3\varphi_{MR}\sqrt{2} \times 100\% \approx 4.24\ \varphi_{MR} \times 100\%$$

The requirements for duplicate analyses are summarized below.

**Duplicate Analyses**

**If $\bar{x}$ < UBGR:**

Statistic: $|x_1 - x_2|$
Warning limit: $2.83\, u_{MR}$
Control limit: $4.24\, u_{MR}$

**If $\bar{x} \geq$ UBGR:**

Statistic: $\text{RPD} = \dfrac{|x_1 - x_2|}{\bar{x}} \times 100\%$
Warning limit: $2.83\, \varphi_{MR} \times 100\%$
Control limit: $4.24\, \varphi_{MR} \times 100\%$

**EXAMPLE**

(UBGR = 5 Bq/kg, $u_{MR}$ = 0.35 Bq/kg, $\varphi_{MR}$ = 0.07)

Suppose duplicate analyses are performed on a laboratory sample and the results of the two measurements are

$x_1$ = 9.0 Bq/kg with combined standard uncertainty $u_c(x_1)$ = 2.0 Bq/kg
$x_2$ = 13.2 Bq/kg with combined standard uncertainty $u_c(x_2)$ = 2.1 Bq/kg

The duplicate results are evaluated as follows.

$$\bar{x} = \frac{9.0 + 13.2}{2} = 11.1 \text{ Bq/kg}$$

Since $\bar{x} \geq 5$ Bq/kg, the acceptance criteria are expressed in terms of RPD.

$$\text{RPD} = \frac{|9.0 - 13.2|}{11.1} \times 100\% = 37.84\%$$

The warning and control limits for RPD are

$$\begin{aligned} \text{Warning limit} &= 2.83 \times 0.07 \times 100\% = 19.81\% \\ \text{Control limit} &= 4.24 \times 0.07 \times 100\% = 29.68\% \end{aligned}$$

In this case, the value of RPD is above the control limit. (Also note that the relative standard uncertainties are larger than the 7% required for concentrations above 5 Bq/kg.)

C.4.2.3 Method Blanks

**Case 1**. If an aliquant of blank material is analyzed, or if a nominal aliquant size is used in the data reduction, the measured blank result is an activity concentration. The target value is zero, but the measured value may be either positive or negative. So, the 2-sigma warning limits are $\pm 2u_{MR}$ and the 3-sigma control limits are $\pm 3u_{MR}$.

**Case 2**. If no blank material is involved (only reagents, tracers, etc., are used), the measured result may be a total activity, not a concentration. In this case the method uncertainty limit $u_{MR}$ should be multiplied by the nominal or typical aliquant size, $M_S$. Then the 2-sigma warning limits are $\pm 2\,u_{MR}M_S$ and the 3-sigma control limits are $\pm 3\,u_{MR}M_S$.

The requirements for method blanks are summarized below.

**Method Blanks**

**Concentration:**

| | |
|---|---|
| Statistic: | Measured concentration |
| Warning limits: | $\pm 2\,u_{MR}$ |
| Control limits: | $\pm 3\,u_{MR}$ |

**Total Activity:**

| | |
|---|---|
| Statistic: | Measured total activity |
| Warning limits: | $\pm 2\,u_{MR}M_S$ |
| Control limits: | $\pm 3\,u_{MR}M_S$ |

**EXAMPLE**

(UBGR = 5 Bq/kg, $u_{MR}$ = 0.35 Bq/kg, $\varphi_{MR}$ = 0.07)

Suppose a method blank is analyzed and the result of the measurement is

$$x = 0.00020 \text{ Bq with combined standard uncertainty } u_c(x) = 0.00010 \text{ Bq}$$

Assuming the nominal aliquant mass is 1.0 g, or $M_S$ = 0.001 kg, the result is evaluated by comparing $x$ to the warning and control limits:

$$\pm\, 2\, u_{MR} M_S = \pm\, 0.00070 \text{ Bq}$$
$$\pm\, 3\, u_{MR} M_S = \pm\, 0.00105 \text{ Bq}$$

In this case $x$ is within the warning limits.

### C.4.2.4 Matrix Spikes

The acceptance criteria for matrix spikes are more complicated than those described above for laboratory control samples because of pre-existing activity in the unspiked sample, which must be measured and subtracted from the activity measured after spiking. The *percent deviation* for a matrix spike is defined as

$$\%D = \frac{\text{SSR} - \text{SR} - \text{SA}}{\text{SA}} \times 100\%$$

where
- SSR is the spiked sample result
- SR is the unspiked sample result
- SA is the spike concentration added (total activity divided by aliquant mass).

However, warning and control limits for $\%D$ depend on the measured values; so, $\%D$ is not a good statistic to use for matrix spikes. Instead we define a "$Z$ score"

$$Z = \frac{\text{SSR} - \text{SR} - \text{SA}}{\varphi_{MR}\sqrt{\text{SSR}^2 + \max(\text{SR}, \text{UBGR})^2}}$$

where "max($x$, $y$)" denotes the maximum of $x$ and $y$. Then warning and control limits for $Z$ are set at ± 2 and ± 3, respectively. (It is assumed again that the uncertainty of SA is negligible.) The requirements for matrix spikes are summarized below.

**Matrix Spikes**

Statistic: $$Z = \frac{\text{SSR} - \text{SR} - \text{SA}}{\varphi_{MR}\sqrt{\text{SSR}^2 + \max(\text{SR}, \text{UBGR})^2}}$$

Warning limits: ± 2

Control limits: ± 3

**EXAMPLE**

(UBGR = 5 Bq/kg, $u_{MR}$ = 0.35 Bq/kg, $\varphi_{MR}$ = 0.07)

Suppose a matrix spike is analyzed. The result of the original (unspiked) analysis is

SR = 3.5 with combined standard uncertainty $u_c$(SR) = 0.29

the spike concentration added is

SA = 10.1 with combined standard uncertainty $u_c$(SA) = 0.31

and the result of the analysis of the spiked sample is

SSR = 11.2 with combined standard uncertainty $u_c$(SSR) = 0.55

Since SR is less than UBGR (5), max(SR, UBGR) = UBGR = 5. So,

$$Z = \frac{\text{SSR} - \text{SR} - \text{SA}}{\varphi_{MR}\sqrt{\text{SSR}^2 + \text{UBGR}^2}} = \frac{11.2 - 3.5 - 10.1}{0.07\sqrt{11.2^2 + 5^2}} = -2.80$$

So, $Z$ is less than the lower warning limit (–2) but slightly greater than the lower control limit (–3).

## C.5 References

Environmental Protection Agency (EPA). 2000. *Guidance for the Data Quality Objectives (DQO) Process*. EPA QA/G-4. EPA/600/R-96/055, EPA, Quality Staff, Washington, DC.

MARSSIM. 2000. *Multi-agency Radiation Survey and Site Investigation Manual* (MARSSIM) Rev. 1. NUREG-1575, Nuclear Regulatory Commission, Washington, DC. EPA 402-R-97-016, Environmental Protection Agency, Washington, DC.

Nuclear Regulatory Commission (NRC). 1998. *A Nonparametric Statistical Methodology for the Design and Analysis of Final Status Decommissioning Surveys*. NUREG-1505. NRC, Washington, DC.